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THE EFFECTS OF RADIATION ON
NICKEL-CADMIUM BATTERY ELECTRODES. II

Mid-Point Report

13 March - 13 June 1964

Prepared for Jet Propulsion Laboratory

Under Contract No. 950514

by

G. R. Argue
H. L. Recht
W. A. McCollum
D. E. McKenzie

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ATOMICS INTERNATIONAL

A Division of North American Aviation, Inc.
P. O. Box 309 Canoga Park, California

Contract: J.P.L. - 950514
Issued: July 29, 1964

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A Division of North American Aviation, Inc.

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Enclosure

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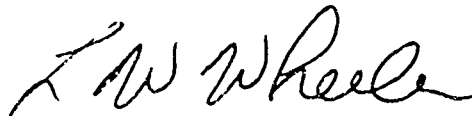
Office of Technical Services
Department of Commerce
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Attention:

Gentlemen:

Pursuant to the request of the Jet Propulsion Laboratory, we are enclosing a copy of the interim report for the Laboratory's study of the effects of radiation on battery electrodes. If you should have any questions concerning this interim report, please telephone Mr. C. R. Caldwell at the Jet Propulsion Laboratory. His telephone number in Pasadena is 354-4321.

Very truly yours,



L. W. Wheeler, Director
Contract Administration
Atomics International Division

Enclosure

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28 p \$5.00 fee
Dr. G. R. Argue

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SUMMARY

→ A study of the effects of gamma radiation on nickel-cadmium cells was continued⁽¹⁾ with emphasis on the loss in capacity of the cadmium electrode and on the radiolysis of the aqueous KOH electrolyte. The previously reported loss of cadmium electrode capacity⁽¹⁾ was confirmed. A total average gamma dose of 9.0×10^7 rads (H_2O) caused a cadmium electrode, being cycled near 75 per cent of full charge, to lose about 15 per cent of its original capacity. The same dose caused essentially no loss in capacity of a fully charged cadmium electrode. A blank cell run at $45^\circ C$, the temperature inside the Co-60 source, showed no loss of capacity, indicating that this is not a temperature effect. Several attempts to restore the lost capacity were unsuccessful. It is tentatively concluded that gamma radiation causes an irreversible inactivation of some of the oxidized species, $Cd(OH)_2$, on the cadmium electrode.

Experiments were carried out to study the radiolysis of aqueous KOH solutions at concentrations from 0.5 per cent to 40 per cent. Hydrogen and oxygen were evolved in a ratio of approximately 2:1 by volume at a concentration of 0.5 per cent KOH. At concentrations from 10 per cent to 40 per cent, the amounts evolved of both gases were considerably reduced, with the oxygen being undetected in most samples. A mechanism is proposed to explain these results.

Radiolysis of 30 per cent KOH containing a portion of a nickel electrode produced relatively large amounts of oxygen whereas only hydrogen was evolved during the irradiation of a similar solution containing a portion of a cadmium electrode. The proposed mechanism is used to explain these results also.

I. INTRODUCTION

The purpose of this project is to study nickel-cadmium battery electrodes in radiation fields to discover how they are affected and the mechanisms involved. A report titled, "The Effects of Radiation on Ni-Cd Battery Electrodes. I" issued February 6, 1964,⁽¹⁾ covers the exploratory studies of these electrodes in neutron, gamma and electron radiation fields.

The present program was directed toward the study, using gamma irradiation, in more detail of those phenomena observed during the exploratory study. Specifically, experiments related to the capacity of the cadmium electrode were made (a) to confirm the observed loss in capacity of the Cd electrode, (b) to determine whether this loss was due to the radiation and/or elevated temperature, and (c) to determine whether the state of charge of the cadmium electrode was a factor in this loss in capacity.

Radiolysis experiments were designed to determine (a) the products of radiolysis of the pure electrolyte, (b) the effect of the electrode materials on these products, and (c) possible mechanisms to explain the products observed. The following interim report describes these experiments and the results obtained.

II. EXPERIMENTAL

A. CADMIUM ELECTRODE CAPACITY STUDIES

Electrodes from Gulton type VO .8 cells were used because of their size and convenience in handling. Cell capacity measurements were carried out in the quartz lined stainless steel cell (Figure 1) as described previously.⁽¹⁾ As the standard procedure for determining capacity or ampere hour capability of a cell, the latter was measured, at room temperature, before and after irradiation by fully charging the cell and then measuring the ampere hours delivered on discharge to 0.2 v below the knee of the discharge curve. As a constant current of 0.2 amp was used for all charge and discharge runs, the capacity can be expressed in minutes. (See later reference to Table I.)

In order to study effects on cadmium electrode capacity, the cadmium electrode was made the limiting electrode using two different types of experiments. In the first type two nickel electrodes were used. The cell size required that these two electrodes touch each other. This close proximity of the two electrodes made it difficult to extract charge from the inner sides of the electrodes due to concentration polarization and the diffusion kinetics. Nevertheless, this method was used with fair success in Run #A-1. The second approach to making the cadmium electrode limiting was to cut about one-third off the cadmium electrode. This was the more successful technique and was used in Runs A-2 through A-4 (see Table I).

The cells with the Cd electrode limiting were charged and discharged completely several times to get an accurate value for the Cd electrode capacity. A current of 0.2 amps for 110 minutes (150 minutes in Run A-1)

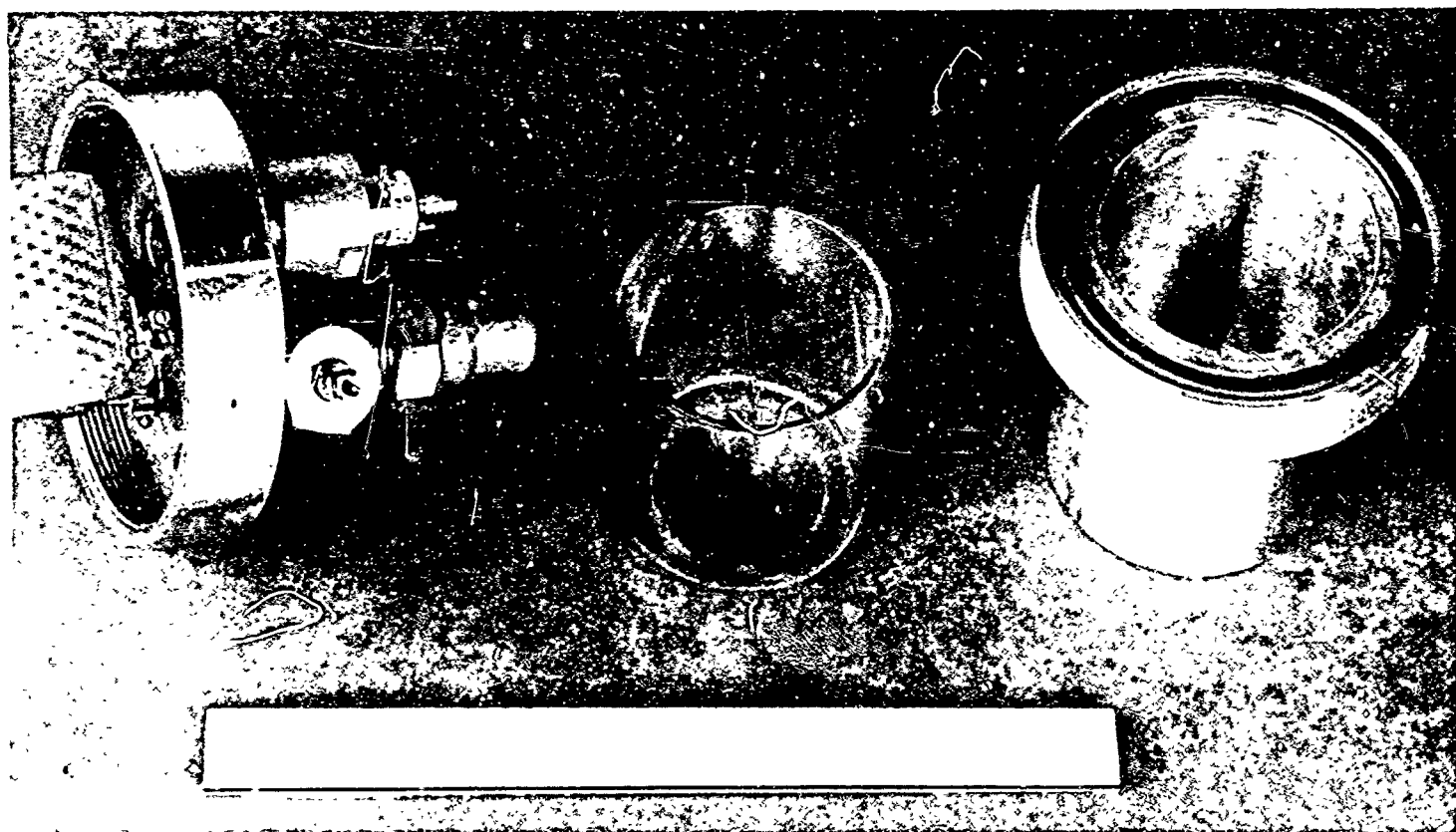


Figure 1. Stainless Steel Cell with Quartz Liner for Cell Irradiations

was found to charge the cadmium electrode to a voltage high enough to generate hydrogen on overcharge. This current and time schedule were used for charging all the cells before and after the experiments regardless of whether the cell indicated overcharge earlier or not.

After the capacities of the cells were measured, the cells were charged at 0.2 amps to full capacity. In Runs A-1, A-3, and A-4 the cells were then discharged to 75 per cent of full charge while in Run A-2 the cell was left at full charge. All the cells were then run at a constant current of 0.2 amp through a cycle of 6 minutes discharge, 4 minutes open circuit, 6 minutes charge, and 4 minutes open circuit for 24 hours prior to irradiation and the cycling was continued during the irradiation.

In an attempt to restore lost capacity, after Run A-3, the cell, at room temperature, was fully charged and then a trickle charge of 0.050 amp passed through the cell overnight. The cell was then completely discharged and recharged several times in succession. Finally, the cell was cycled at 75 per cent of full charge for 24 hours.

B. RADIOLYSIS OF AQUEOUS KOH

Various concentrations of aqueous KOH solution from 0.5 per cent to 40 per cent were irradiated in the Co-60 gamma source to determine the radiolytic products and their dependence on the concentration of KOH. Several runs using 30 per cent KOH (the concentration used in almost all the nickel cadmium cell work) in contact with either a nickel or a cadmium electrode were made to determine the effect of the electrode material on the radiolysis process. The first irradiations were carried out in a quartz lined stainless steel cell with an air cover, as shown in Figure 2. A pressure transducer to measure pressure changes during irradiation, and

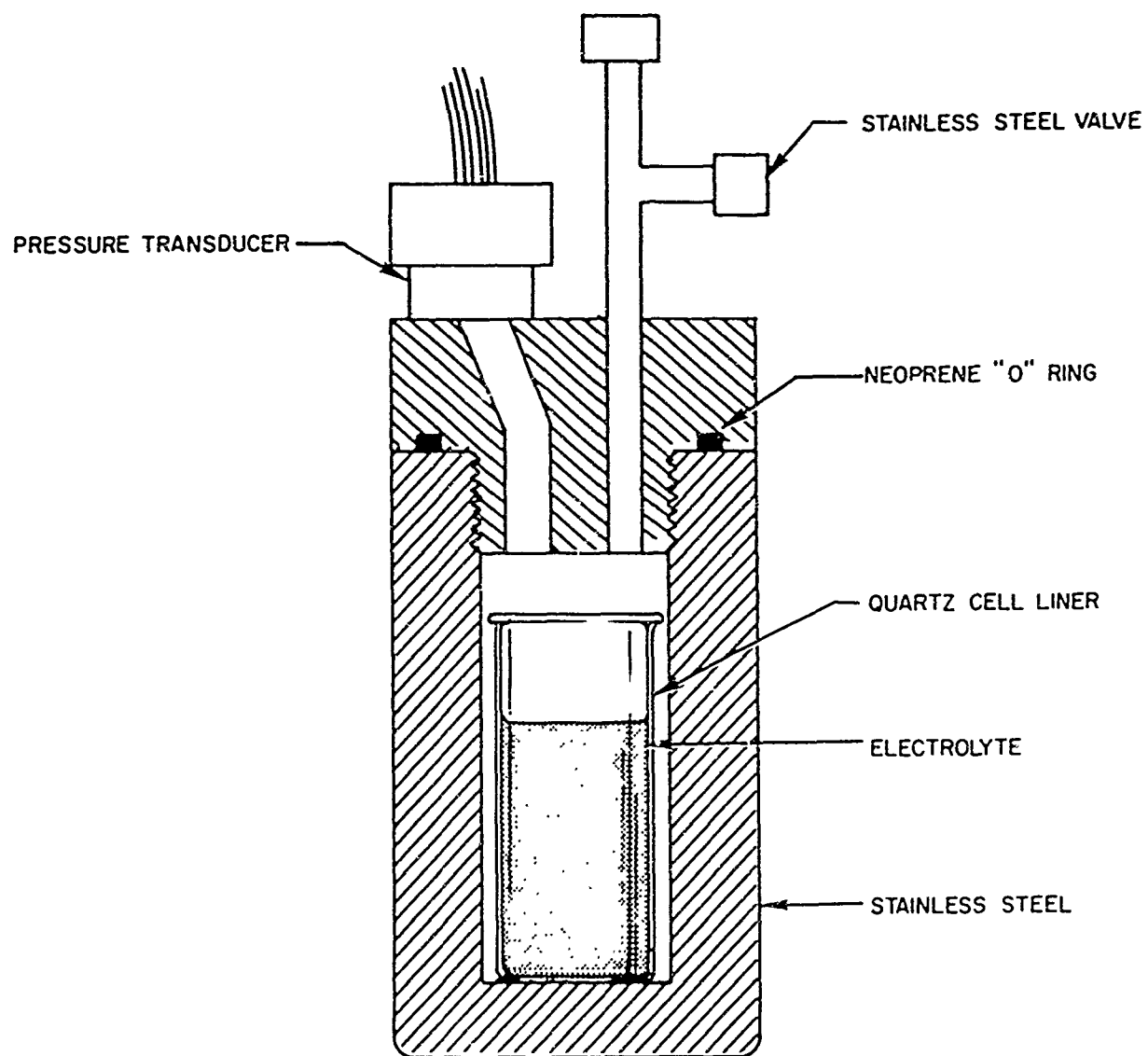


Figure 2. Stainless Steel Cell with Quartz Liner for Radiolysis Experiments

a stainless steel needle valve for removing gas samples were incorporated in the top of this cell. The possibility of interaction of the hydrogen and oxygen produced by radiolysis with the stainless steel, the neoprene "O" ring, or other component, and the observation that CO was evolved in one run prompted a change in the cell design. The new all-quartz cell is shown in Figure 3. Figure 3a shows the cell prior to filling. Figure 3b shows the cell after sealing. The electrolyte was put in through the open tube (Figure 3a). The cells were evacuated and back-filled with helium four times before sealing the open tube. The break-off tip of the cell facilitated removal of the gas for analysis. (See Table II.)

The cells, after gas analysis, were left under negative pressure. Analysis was then carried out for peroxide in the electrolyte. This was done by taking aliquots of the solution, diluting them with H_2SO_4 , and adding ceric sulphate. The amount of ceric ion converted to cerous by the peroxide was measured with a Beckman DU spectrophotometer with a sensitivity for peroxide of $1 \mu\text{g}/\text{cc}$.

Similar cells were used to study the effect of electrode material on the products of the radiolysis of KOH. The electrodes were cut in strips and slipped into the cell through the narrow opening. Duplicate runs were made in all cases. In order to separate temperature effects from radiolysis effects, some duplicate cells were run for the same time without irradiation in the 45°C constant temperature bath. Two cells were irradiated containing 1 per cent peroxide in 30 per cent KOH to check on the peroxide stability. (See Table III.)

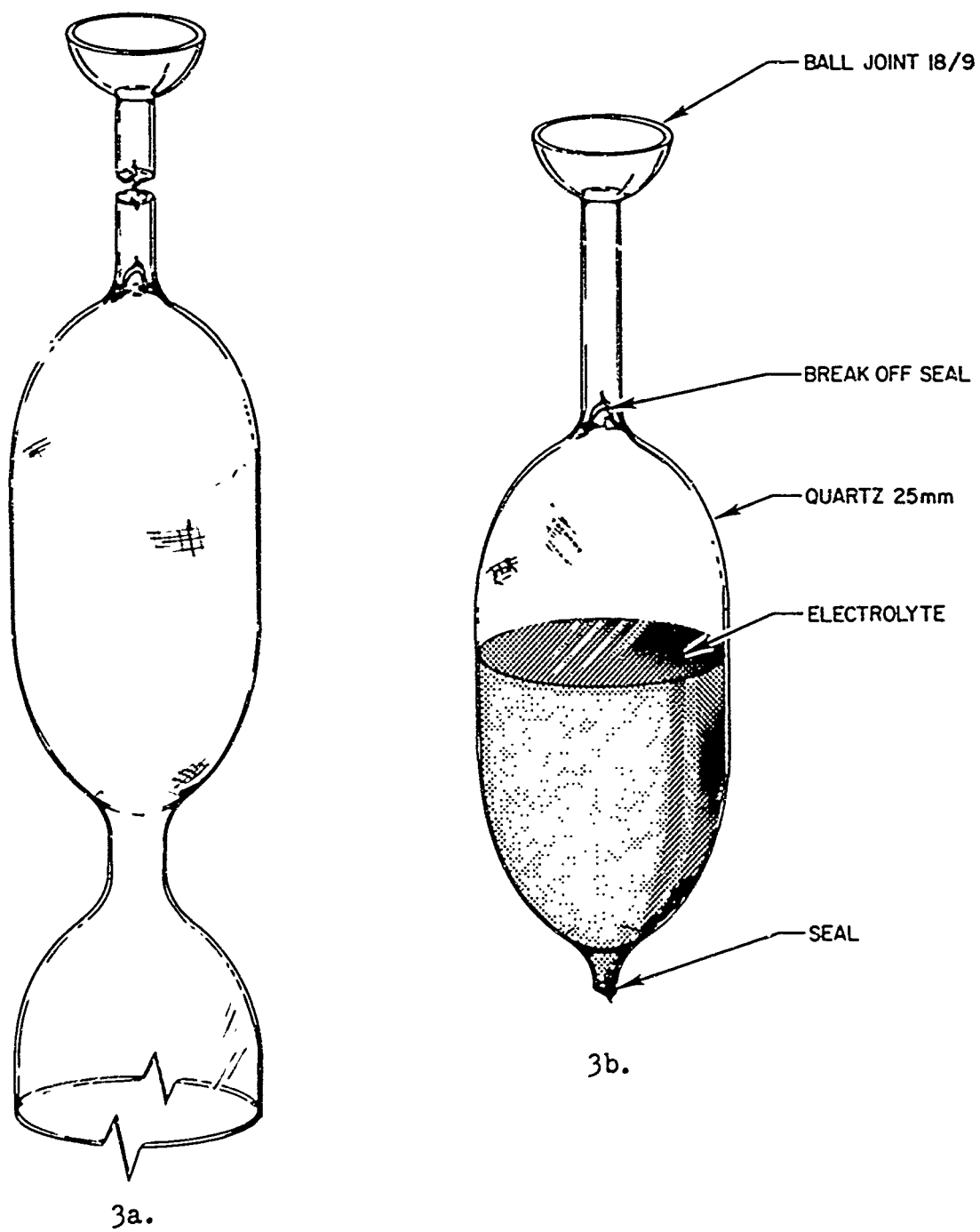


Figure 3a. Quartz Capsules for Radiolysis Experiments
 3b. Capsule Filled and Sealed

III. RESULTS

A. CADMIUM ELECTRODE CAPACITY

The results of these experiments are summarized in Table I.

TABLE I. RESULTS OF CADMIUM ELECTRODE CAPACITY EXPERIMENTS

Run #	Cell Temp.	Time (Hrs)	Total Dose in Rads (H ₂ O)	% Charge	Initial Capacity (Min. at 0.2 amp)	Final Capacity (Min. at 0.2 amp)	% Change
A-1	45°C	63	8.7×10^7	75	134	112	16.5
A-2	45°C	65	9.2×10^7	100	90	87	3.3
A-3	45°C	65	9.2×10^7	75	107	92	14.0
A-4	45°C	68	none	75	99	97	2.0

The average loss in capacity of the cadmium electrode of about 15 per cent is significant. Data on Run A-2 indicate that at essentially full charge the Cd electrode was practically unaffected by gamma radiation. Also, the data on Run A-4 show that the effects observed in Runs A-1 and A-3 were not due to temperature.

Several methods (see p. 5) were tried after Run A-3 in an attempt to restore the lost capacity. None of these were successful, within experimental error (~3%), in restoring any of this lost capacity.

In the course of these capacity studies, the voltage of the Cd electrode was observed to decrease by approximately 10 mv in a step fashion at some point during the initial discharge of the cell (at room temperature) after the irradiation and the blank temperature experiments (at 45°C). Figure 4 shows typical initial discharge curves at room temperature. This effect was absent during the subsequent capacity measurements which were also made at room temperature.

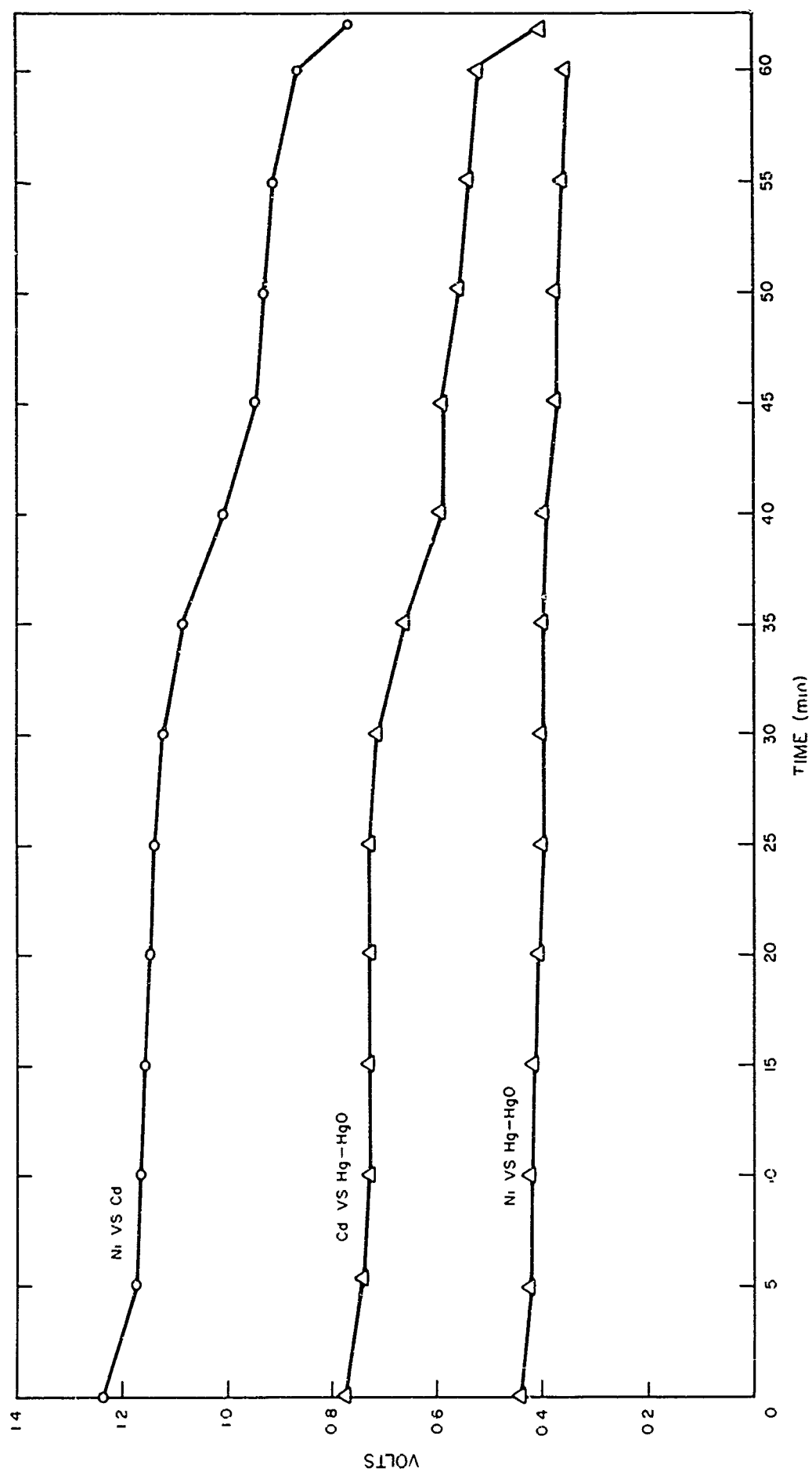


Figure 4. Initial Discharge Characteristics of Cadmium Limiting Ni-Cd Cell
After 65 hours at 45°C

B. RADIOLYSIS OF KOH SOLUTIONS

The results of radiolysis of aqueous KOH solutions are given in Table II. The radiolysis results of such solutions in the presence of electrodes or added H_2O_2 are shown in Table III.

TABLE II. RADIOLYSIS PRODUCTS FROM CO-60 GAMMA IRRADIATIONS OF
VARIOUS CONCENTRATIONS OF KOH¹

Run #	% KOH	% H_2	% O_2	% N_2 ²	Cover Gas	Sample System ³ Pressure (mm)
R-8-9	0.5	22.4	12.0	0.04	He	56
R-8-F	10	0.8	0.16	0.3	"	19
R-6-1	10	2.2	0	0.34	"	22
R-6-2	20	5.9	0	0.31	"	28
R-6-3	20	3.5	0	0.77	"	28
R-8-C	30	2.0	0.8	4.0	"	39
R-8-D	30	4.1	1.5	4.1	"	19
R-8-2	40	5.9	2.0	0.2	"	21
R-3	30	5.3	13.7	81	Air	101 ⁵
R-2 ⁴	30	7.8	17.3	75	"	171 ⁵

1. Total dose 6.6×10^7 rads.
2. With He cover gas, N_2 indicates residual air left after He flush. The amount of this residual air was high in Runs R-8-C and R-8-D.
3. Sample system pressure measured when cell connected to chromatographic sampling system. Variations in this parameter in the runs with He cover gas probably arise from variable expansion of the gas during cell sealing prior to irradiation.
4. Air leakage suspected during analysis.
5. Run is quartz-lined stainless steel cell. Pressure rise of ~1 psi recorded in Run R-3.

TABLE III. RADIOLYSIS¹ PRODUCTS OF 30% KOH
IN PRESENCE OF ELECTRODES AND ADDED REAGENTS

Run #	% KOH	Electrode or Reagent	% H ₂	% O ₂	% N ₂	Cover Gas	Sample System ³ Pressure (mm)
R-8-10	30	Ni	9.3	31.5	0	He	39
R-8-3	30	Cd	16.1	0	0.44	"	21
R-8-7	30	1% H ₂ O ₂	5.0	balance ⁴	0	"	155
R-8-11	30	1% H ₂ O ₂	4.7	balance ⁴	0	"	309
R-8-5	30	Ni ²	0	16.1	1.1	"	17
R-8-6	30	H ₂ O ₂ ²	0	balance ⁴	0	"	74

1. Total dose 6.6×10^7 rads.
2. These samples were not irradiated but rather were stored at 45°C for a period equal to the irradiation time.
3. Sample system pressure measured when cell connected to chromatographic sampling system. Variations in this parameter in the runs with He cover gas probably arise from variable expansion of the gas during cell sealing prior to irradiation.
4. O₂ evolution was occurring during cell sealing procedure, diluting the He cover gas. O₂ partial pressure too high for accurate analysis; estimated to be only gas in sample besides H₂ if reported.

IV. DISCUSSION AND CONCLUSIONS

A. CADMIUM ELECTRODE CAPACITY

From the results shown in Table I one may see that gamma radiation causes a loss in capacity of a partially discharged cadmium electrode. Under the conditions employed, an average loss of 15 per cent occurred with the electrode at 75 per cent of full charge. Run A-2, in which essentially no change of capacity occurred with a fully charged electrode, has not been repeated. However, the results from it indicate that the state of charge is an important parameter in this capacity loss phenomenon.

From previously reported results,⁽¹⁾ it can be established that the actual material lost by sloughing from the Cd electrode is insufficient to account for the loss in capacity. The active cadmium must somehow have become deactivated. With this in mind, several recharging procedures (see p. 5) were tried with the aim of effecting some recovery of this lost capacity, all without success.

These observations raise the question as to the mechanism of this loss in capacity caused by the gamma radiation. There are several possible explanations, none of them substantiated, which may explain this phenomenon. First it should be pointed out that the deactivation appears to affect the oxidized form of cadmium, $(\text{Cd}(\text{OH})_2 \cdot n\text{H}_2\text{O})$, and not, directly, the cadmium metal itself. One possibility is that irradiation results in the formation of a novel species of cadmium hydroxide, oxide, or peroxide which is electrochemically unreactive. It might be speculated that radiation may cause nucleation and crystal growth of the cadmium hydroxide to occur, either by itself or with cadmium metal. These enlarged crystals may lower the amount of surface of active material. If this mechanism were true, the electrode would lose more capacity as the total dose increases. Further

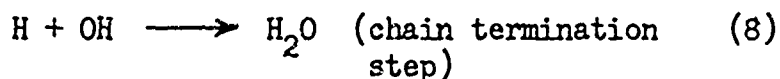
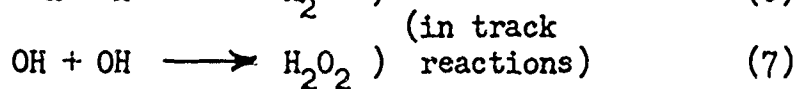
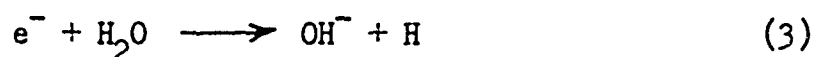
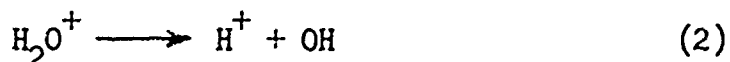
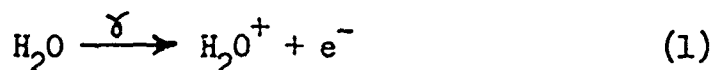
investigation will be required before any definitive explanation of this capacity loss phenomenon may be offered.

As shown by the data from Run A-4 (Table I), cycling at a temperature of 45°C without radiation appears to have little, if any, effect on the capacity of the cadmium electrode, at least at 75 per cent of full charge. This observation is consistent with the manufacturer's data.

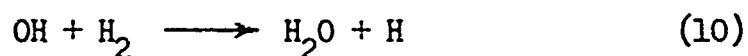
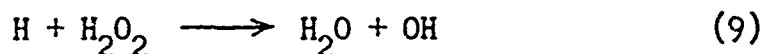
B. RADIOLYSIS OF AQUEOUS KOH

Radiolytic decomposition of air-saturated water produces hydrogen and hydrogen peroxide; in the absence of air, the amount of decomposition is greatly reduced. The mechanism for the radiolysis of water may not apply to the radiolyses of aqueous solution at pH's other than seven, since a different product yield is generally obtained.

An accepted mechanism^(2,3) for the radiolysis of water is:



In the absence of air the following occurs:



As shown in equations (1) through (4), the overall primary decomposition products are H and OH radicals. In the track of the incident photon, where these products are located, there occurs production of H_2 and H_2O_2 , as shown in equations (6) and (7). There is no net production of products, other than water, when the existence of these radicals is terminated by equation (8). In the absence of air (or oxygen) the reaction of radicals with the products of the in-track reactions results in a net removal of these in-track products (equations (9) and (10)). The overall net effect becomes essentially no production of gaseous products in the absence of air.

In the presence of oxygen the following reaction occurs:

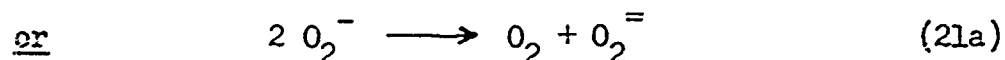
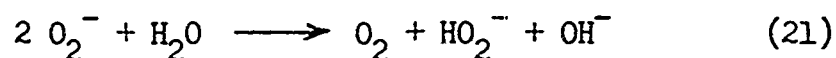
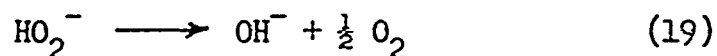
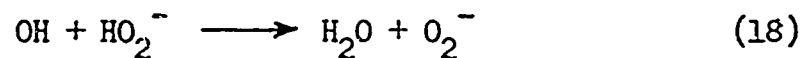
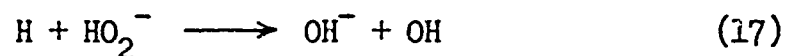
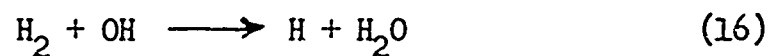
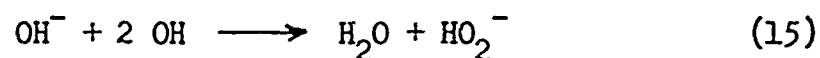


In this case, reaction (9) will be inhibited, and a net amount of peroxide will be formed. A net evolution of hydrogen also occurs because of the resulting imbalance^(2, p.90). These reactions explain the products observed from the radiolysis of water in air or in inert atmosphere.

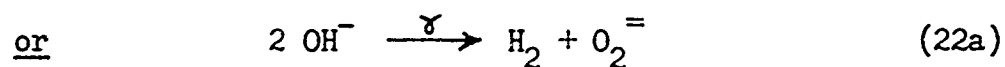
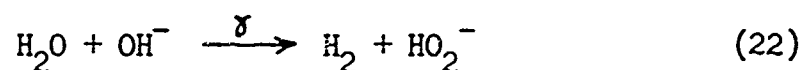
Very few radiolyses data are available for alkaline solutions. Veselovsky⁽⁴⁾ irradiated a 0.3 N NaOH solution which was covered with one atmosphere of oxygen. He reported peroxide formation with a steady state concentration of 10.2 μg per milliliter. This is consistent with the above mechanism, since the presence of oxygen above the solution promotes peroxide formation as in equation (11). He did not report any hydrogen

formation. Czapski and Dorfman⁽⁵⁾ reported some pulse radiolysis studies of aqueous solution covering the pH range of 2 to 14. Above a pH of 10, using a UV spectrophotometer, they observed the formation and decay of two new species, which they suggested were O_2^- and $O_2^{=}$. The half-lives of these species were observed to be pH dependent.

Radiolysis in strongly basic solutions probably proceeds by a mechanism involving OH^- and differing from that given above. As reported (Table II) we found that at low concentration of KOH, namely, 0.5 per cent, both hydrogen and oxygen were evolved in a ratio of almost 2:1. At higher concentrations of KOH, from 10 per cent to 30 per cent, only hydrogen was evolved. At 40 per cent KOH, about 2 per cent oxygen was observed, but further work is needed to confirm this result. A solution of 1 per cent H_2O_2 in 30 per cent KOH was shown to be unstable in the gamma field as the amount of oxygen evolved corresponds to essentially complete decomposition of the peroxide. Examination of the radiolysis mechanism above shows that the yield of hydrogen should decrease owing to a probable increased OH concentration (reaction (10)) due to the reaction $OH^- \xrightarrow{\gamma} OH + e^-$ (see equation (12) below). Likewise, equation (7) shows that this probable increased yield of OH should result in peroxide formation in air-free solution. A radiolysis mechanism for basic solutions should be consistent with these facts. Of several possible mechanisms,^(2,6) the following appear most reasonable in explaining our results.



with the overall reaction being either



Equations (12) through (15) show the primary reactions and products postulated for the radiolysis of aqueous alkaline solutions. Equations (16) through (19) show how these primary products can interact with each other to form oxygen gas and the O_2^- species. Equation (20) shows a step which allows for removal of oxygen from the system and explains why oxygen is absent from or present only in small quantity in the radiolysis products in the more concentrated KOH solution. The processes shown in the equations above indicate that the amount of hydrogen evolved should depend on the OH^- concentration. The data in Table II show that, indeed, the amount of hydrogen evolution is higher at the lowest KOH concentrations studied.

In basic solution, H_2O_2 is thought generally to exist as HO_2^- . However, Czapski and Dorfman⁽⁵⁾ have proposed the existence of $\text{O}_2^{=}$ at pH 14. Equations (21) and (21a) correspond, respectively, to the existence of HO_2^- and $\text{O}_2^{=}$ as the predominant hydrogen peroxide species in our solutions. Likewise, the postulated overall process would be given by Equations (22) and (22a), respectively. (Each of the equations involving HO_2^- may be written with $\text{O}_2^{=}$ as the species present.) We were unable to confirm the presence of $\text{O}_2^{=}$ in our solutions.* It is also possible that the $\text{O}_2^{=}$ decomposed during the time between radiolysis and analysis, or during the transfer of the solution from the radiolysis cell to the spectrophotometer cell. Any $\text{O}_2^{=}$ or HO_2^- neutralization with acid should form H_2O_2 during the chemical analysis for peroxide. The concentrations of these species must be small, since standard runs in the laboratory using the ceric method were capable of detecting 1 $\mu\text{g}/\text{cc}$ ($G = 0.3$ molecules/100 ev). No peroxide was ever detected in the radiolyzed samples.

C. RADIOLYSIS OF AQUEOUS KOH IN CONTACT WITH ACTIVE MATERIALS

Hydrogen and oxygen were the products of radiolysis of a solution of 30 per cent KOH in contact with a 75 per cent charged nickel electrode (Table III). The concentration of hydrogen in the gas phase was about 9 per cent and is thus about four times the amount of hydrogen evolved from 30 per cent KOH solution alone (calculated from the hydrogen partial pressures found in the gas from Runs R-8-10, R-8-C, and R-8-D). The oxygen concentration in the gas phase from this run was about 30 per cent whereas essentially no oxygen was detected in the products of radiolysis

*In 30 per cent KOH the quartz cells of the spectrophotometer became etched rapidly so that the beam is diffuse making the spectrum meaningless. Another approach is needed to detect $\text{O}_2^{=}$ in such strong KOH solutions.

of the pure 30 per cent KOH solution (allowing for oxygen from entrapped air which can be calculated from % N_2). Oxygen was evolved to the extent of 16 per cent in a cell containing 30 per cent KOH and the nickel electrode, at 75 per cent of charge, run as a blank at 45°C for 48 hours without irradiation. The same time was used for the radiation runs to give a total dose of 6.6×10^7 rads (H_2O). The similar run (R-8-10) with irradiation yielded 4.5 times this amount of oxygen, (calculated from oxygen partial pressures in these runs). Reduction of the nickel electrode probably accounts for all the oxygen evolved in the 45°C run although this fact was not verified. The likely reaction would be $2 NiOOH + H_2O \longrightarrow 2 Ni(OH)_2 + \frac{1}{2} O_2$. This reaction probably also occurs in the irradiated cell. To explain the higher oxygen concentration found, either this reaction is occurring at a higher rate or another reaction is affected. This latter may be the reaction shown in equation (19) where the nickel electrode catalyzes the peroxide decomposition. Previous experiments⁽¹⁾ showed that a charged nickel electrode did contribute to the decomposition rate of peroxide in 30 per cent KOH even at room temperature. This fact is consistent with the results above.

The presence of a 75 per cent charged cadmium electrode in 30 per cent KOH during an irradiation causes hydrogen to be produced. The concentration of hydrogen found in the gaseous product, 16 per cent, is considerably higher than that found in the products from the radiolysis of pure 30 per cent KOH. No oxygen was found. This is to be expected as the cadmium metal in the cadmium electrode is known to combine with oxygen rapidly in oxidizing the electrode. The mechanism proposed to explain the high hydrogen concentration consists of the stepwise reaction of cadmium with

hydroxyl radicals: e.g., $\text{Cd} + \text{OH} \longrightarrow \text{CdOH}$ and $\text{CdOH} + \text{OH} \longrightarrow \text{Cd}(\text{OH})_2$.

These reactions would inhibit the reaction shown in equation (16) and thus result in the net production of more hydrogen. (As this process involves the cadmium metal itself, it is not the one causing irreversible loss in cadmium electrode capacity.) An experiment to help prove this mechanism would be to irradiate 30 per cent KOH containing a fully discharged cadmium electrode. In this case only the normal 2-4 per cent hydrogen as evolved from pure 30 per cent KOH should be produced, assuming the nickel plaque has no effect.

Hydrogen peroxide in 30 per cent KOH does not appear to be stable even at room temperature. Several samples containing 30 per cent KOH + 1 per cent H_2O_2 were prepared in the laboratory. Gas evolution occurred immediately although not nearly as fast as when a nickel electrode was present. The oxygen concentration in the gas samples of both the irradiation and elevated temperature blank were essentially the same, indicating complete decomposition of the peroxide. The ceric analysis also failed to show any residual peroxide present. These results on the instability of H_2O_2 are consistent with our inability to detect H_2O_2 in our radiolyzed samples within the limits stated previously.

V. FUTURE PLANS

A few additional radiolysis studies are planned for the next period to duplicate unconfirmed data. No runs beyond these are planned as a rather extensive investigation would be required to verify the plausible mechanisms proposed.

The relation of state of charge to loss of capacity of the cadmium electrode during radiolysis will be studied further to define its nature. The experiments to determine the relationship of state of charge to the capacity loss of the cadmium electrode will be carried out in a compartmented cell so that the amount of material sloughed from each electrode may be determined. A porous quartz section in the cell will separate the electrodes.

The effect of gamma radiation on nickel cadmium cells of different manufacturers will also be studied in a preliminary fashion to determine the differences in observed effects due to the manufacturing method. Of primary interest will be the effects of voltage, capacity and material loss from electrodes.

Voltammetric studies of the nickel-cadmium system in gamma radiation fields are also planned. Small electrodes, reduced in size by cutting, will be employed to permit polarization to occur with available current sources. The experience gained during the present work has shown that this cutting procedure has no effect on the behavior of the electrodes.

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